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Femtosecond laser induced crystallization of hydrogenated amorphous silicon for photovoltaic applications

Andrey V. Emelyanov^{a,*}, Mark V. Khenkin^a, Andrey G. Kazanskii^a, Pavel A. Forsh^{a,b}, Pavel K. Kashkarov^{a,b}, Mindaugas Gecevicius^c, Martynas Beresna^c, Peter G. Kazansky^c

^a Physics Department, Lomonosov Moscow State University, Moscow, 119991, Russia

^b National Research Centre “Kurchatov Institute”, Moscow, 123182, Russia

^c Optoelectronics Research Centre, University of Southampton, Southampton, Hampshire, SO17 1BJ, UK

*e-mail: av.emelyanov@physics.msu.ru

Abstract

Femtosecond laser assisted crystallization is used to produce nanocrystalline silicon from hydrogenated amorphous silicon. Changes in structural, optical, electrical and photoelectric properties of laser modified amorphous silicon were investigated. Laser treated films were characterized using atomic force microscopy, Raman spectroscopy, constant photocurrent method and current measurements. Crystalline volume fraction as well as conductivity of laser irradiated films increased with the applied laser fluence, while hydrogen concentration in the films was found to decrease with the fluence. Spectral dependences of absorption coefficient, measured by constant photocurrent method, are discussed in terms of hydrogen out-effusion and additional defect states formation in silicon films during the laser treatment.

1. Introduction

Laser induced crystallization of hydrogenated amorphous silicon (a-Si:H) is one of the preferred methods of microcrystalline silicon ($\mu\text{c-Si}$) thin film formation for applications in thin-film electronics [1] and photovoltaics (PVs) [2]. Despite both nanosecond and femtosecond laser pulses can be used for a-Si:H crystallization [3, 4], femtosecond laser-induced crystallization includes a non-thermal ultrafast phase transition followed by a thermal effect process which is different from rapid thermal melting and subsequent solidification made by nanosecond laser pulses [5, 6].

Most of recent studies, devoted to femtosecond laser-induced crystallization of a-Si:H, were focused on investigation of structural properties of laser treated films [4 – 10]. It was found that the laser treatment of a-Si:H film not only changes its internal structure (crystallization process [7, 8]), but also significantly influences the surface of the film leading to the submicron spikes formation (see, e.g., [4, 9]). In turn, the spikes result in a decrease of the reflection and in a substantial increase of the optical absorption coefficient in the quanta energies region below 1.8 eV [9, 10]. Additionally, a-Si:H film treated by femtosecond laser radiation in air shows down-shifter luminescent features [11]. Both indicated effects can be used to increase the efficiency of tandem μ c-Si / a-Si:H solar cells, obtained by a-Si:H laser treatment.

Electrical and photoelectric properties of femtosecond laser modified a-Si:H films are studied in a less substantial extent than structure transformations, despite they are very important for optoelectronic applications of modified silicon films. Preliminary investigations of electrical and optical properties of a-Si:H films treated by femtosecond laser pulses revealed some peculiarities [12, 13]. Namely, as a result of crystallization the substantial increase in the dark conductivity was observed for the laser treated films [12]. However spectral dependences of absorption coefficient of treated a-Si:H films measured by constant photocurrent method were unexpectedly corresponded to that of a-Si:H even for highly enough (~30 %) crystallized films [13]. This result remains puzzling while presenting a possible key to understanding photoelectric properties of the material and poor performance of devices based on it [14]. To address the issue in this work we have extended our previous research to the microscopy and hydrogen concentration studies and switched contacts configuration. This allowed us to explain film's photoelectric properties in terms of hydrogen effusion and defect states formation in irradiated films during the laser processing. The results pointed out that hydrogen deficiency in femtosecond laser treated a-Si:H films needs to be overcome in order to obtain high quality material for PVs.

2. Experimental details

300 nm thick a-Si:H films were deposited on silica glass substrates by plasma-enhanced chemical vapour deposition upon the decomposition of silane (SiH_4) and argon (Ar) gas mixture at the substrate temperature of 250 °C. The volume ratio between the gases in the reaction chamber corresponded to 25% SiH_4 and 75% Ar. Ultrafast laser treatment of a-Si:H films was carried out with Yb:KGW based femtosecond system (Pharos, Light Conversion Ltd.) that delivered pulses of 500 fs with repetition rate of 200 kHz and wavelength centered at 1030 nm. The laser beam was focused via the aspheric lens with a numerical aperture of 0.16. The focal plane was placed 80 μm above the sample surface in order to increase the laser irradiation area

and avoid surface ablation. The laser spot had a Gaussian profile with the diameter of about 15 μm on the film surface. The samples were irradiated by continuously scanning with the translation speed of 5 mm/s. The scanning step was 2 μm . The highest laser fluence used in the experiments was 60 mJ/cm^2 . Using higher fluences ($\geq 70 \text{ mJ}/\text{cm}^2$) led to film surface oxidation as the laser processing was carried out in ambient air atmosphere.

Films surface studies were carried out by means of atomic force microscopy (AFM, microscope Veeco MultiMode 4). The structure of the irradiated samples was examined with micro-Raman spectrometer (Horiba Jobin Yvon HR800). Electrical and photoelectric measurements were carried via aluminum contacts deposited on the film surface perpendicularly to the beam scanning direction. In contrast to [12, 13] this geometry of the contacts allowed us to decrease the influence of non-modified part of the film on the obtained results. Distance between contacts and their length were 0.5 and 4 mm correspondingly. The measurements of conductivity, photoconductivity and spectral dependences of the absorption coefficient were carried in vacuum at a residual pressure of 10^{-3} Pa after annealing of the film at the temperature of 170 $^{\circ}\text{C}$ for 10 min. Photoconductivity $\Delta\sigma_{ph} = (\sigma_{ill} - \sigma_d)$ was measured with intensity of the light 2 mW/cm^2 and quanta energy 1.8 eV, where σ_d and σ_{ill} – dark conductivity and conductivity under illumination correspondingly. The spectral dependences of absorption coefficient (α_{CPM}) were characterized by constant photocurrent method (CPM) [15].

3. Results and discussion

AFM images of amorphous silicon film surfaces before and after film treatment with the laser fluence of 60 mJ/cm^2 are shown in the Fig. 1. One can see from the figure that surface submicron size spikes have been created upon laser treatment. The spikes are formed into stripes along the direction of laser beam scanning. It is worth pointing out that stripes of spikes appeared despite we used the 87% laser spot overlapping in our experiments. The stripes are spaced from each other roughly by 2 μm matching the scanning step of the laser beam used for the film treatment. This unexpected result opens the possibility of a-Si:H film precise surface structuring using wide laser beam spot. Stripes formation is attributed to the Gaussian distribution of the laser intensity and is caused apparently by sharp dependence of spikes formation on laser fluence.

AFM measurements of film surface profiles (Fig. 1) revealed spikes with heights of 15 – 40 nm formed after laser irradiation with the fluences of 30 – 60 mJ/cm^2 . Several processes have been identified which influence the surface structure of amorphous silicon film, crystallized by laser irradiation: hydrogen out-diffusion from a-Si:H [16], multiple shot crystallization [17], differences in latent heat and thermal conductivity between crystalline and amorphous silicon

[18], and ambient condition of the irradiation atmosphere [17]. Explosive evaporation of hydrogen is expected to be the main reason for surface structures to occur [5, 17].

The crystalline volume fraction in silicon films under study was determined from Raman spectra analysis (Fig. 2). It is worth noting that the beam spot diameter of Raman excitation laser was larger than the average width of the modified stripes on the film surface detected by AFM measurements. Therefore, Raman analysis provides surface-averaged information of the film structure. A pronounced peak near $\omega_A = 480 \text{ cm}^{-1}$ is observed clearly on spectra of all samples. The peak corresponds to the amorphous silicon transverse-optical (TO) vibration mode [19]. Another peak observed around $\omega_C = 520 \text{ cm}^{-1}$, corresponding to the crystalline silicon TO mode [20], appears on the Raman spectra for the samples treated with the laser fluences above 50 mJ/cm^2 . The integrated intensity of the peaks around 480 and 520 cm^{-1} were measured to estimate the crystalline volume fraction f_C in studied films as described in [12, 13] (Fig. 3). One can see from the Fig. 3 that while increasing laser fluence crystalline volume fraction grows, reaching the maximal value of about 36 %.

The inset in Fig.2 shows the Raman peak observed around 625 cm^{-1} . This peak is due to presence of hydrogen in the film and corresponds to wagging vibration of Si-H bonds [21]. We used this peak to estimate the change of H concentration in our films after laser treatment. Fig. 3 shows relative change of hydrogen content in the film as a function of laser fluence calculated from integrated intensities of the Si-H vibration peaks. One can see from the inset that intensity of the peak at 625 cm^{-1} decreases with the increase of laser fluence. This is due to enhancement of hydrogen effusion from the film with increase of laser fluence. It is well known, that hydrogen atoms passivate dangling bonds in hydrogenated silicon films. Therefore if the process of film crystallization is accompanied by hydrogen out-effusion, the dangling bonds concentration in modified stripes of a-Si:H film would increase. The increase of dangling bonds concentration has to result in decrease of charge carriers lifetime and photoconductivity of modified stripes of the film. Thus the measured photoconductivity of the film has to be determined by unmodified parts of silicon film.

Structural changes caused by femtosecond laser treatment of a-Si:H films led to changes in their electrical and photoelectric properties. According AFM analysis our laser treatment procedure results in inhomogeneous structure transformation across the surface of the film. Therefore it is worth to note that we will present below averaged electrical and photoelectrical parameters. The dependences of dark conductivity and photoconductivity of the samples at room temperature as functions of used for treatment laser fluence are shown in Fig. 4. The figure shows that dark conductivity increases dramatically by 6 – 7 orders of magnitude for the sample

treated with the laser fluence of 50 mJ/cm^2 . It is well known that dark conductivity of $\mu\text{c-Si}$ exceeds that of a-Si:H by 4 – 6 orders of magnitude [22]. So the abrupt increase of the dark conductivity could be explained by increase of nanocrystalline part of the film contribution to charge carriers transport path through the film. According to theoretical calculations for randomly distributed silicon nanocrystals inside the sample the carriers transport path changes when crystalline volume fraction exceeds the percolation threshold, which is around 16% for the infinite systems [23]. Our measurements show that 13.4 % crystallinity of the sample treated with the laser fluence of 50 mJ/cm^2 is high enough to reach the percolation threshold. Lower value of obtained percolation threshold is most likely determined by stripes formation and non-uniform distribution of Si nanocrystals. The area along the stripe made by the laser beam center seems to be preferential for charge carriers path. Fig. 4 shows that photoconductivity increases slightly for the films treated with higher laser fluences and reaches the maximum value for the film with 13.4 % crystallinity (treated with laser fluence 50 mJ/cm^2). Some decrease of $\Delta\sigma_{ph}$ for the film treated at higher fluence is most likely connected with macroscopic defects formation in the treated film due to the processes of spallation [13] and hydrogen out-effusion.

High dark conductivity of femtosecond laser crystallized a-Si:H has been the most desirable feature for thin film electronics. While in the context of PVs, it is stated that the dark conductivity should be less than 10^{-10} S/cm and photoconductivity should be greater than 10^{-6} S/cm for device quality amorphous and microcrystalline silicon [24]. In order to utilize the desirable properties of laser treated a-Si:H films for PVs, their dark conductivity needs to be reduced and photoconductivity needs to be increased. As hydrogen is playing a key role in dangling bonds passivation, the minimization of the hydrogen effusion from the film during the femtosecond laser processing may be one of the methods of addressing this problem. To minimize the hydrogen effusion one have to sort out appropriate laser treatment parameters such as pulse duration, repetition rate, scanning speed, etc.

Spectral dependences of absorption coefficient $\alpha_{\text{CPM}}(h\nu)$ obtained by the constant photocurrent method are shown in Fig. 5. For all treated films the shape of $\alpha_{\text{CPM}}(h\nu)$ corresponds to that of hydrogenated amorphous silicon: exponential rise in the range of photon energies $1.4 \text{ eV} < h\nu < 1.8 \text{ eV}$, which is attributed to optical transitions from bands tails states, and so called “absorption shoulder” at $h\nu < 1.4 \text{ eV}$, which is attributed to transitions from defect (dangling bonds) states to conduction band [25]. It is well known that the shape of absorption spectrum changes while the transition from a-Si:H to $\mu\text{c-Si}$ structure takes place [26]. However CPM spectrum of the films treated with different fluences does not exhibit such change. It is also noticeable that an “absorption shoulder” increased after treatment with the fluence of 30 mJ/cm^2 ,

while further increase of the laser fluence did not lead to additional defect states formation. In contrast to [13] as noted above used laser scanning direction allowed us to follow easily the influence of laser-induced structure modification on measured parameters of the film.

Hydrogen effusion from the film is increasing defects concentration and thus leads to the increase of absorption below 1.4 eV. However, sharp change of absorption in a defect region of CPM spectrum (Fig. 5) does not correlated with monotonic decrease of hydrogen concentration (Fig. 3) as the laser fluence is increasing. We believe that inhomogeneous structure transformation of the samples by femtosecond laser radiation is the main reason of the obtained discrepancy. Hydrogen out-effusion as well as film crystallization occurs non-uniformly during the laser beam scanning. The intensity in the center of the laser beam reaches the maximum, what leads to the structural changes located predominantly in the central part of the beam spot (Fig. 1). Therefore both hydrogen out-effusion, subsequent creation of defect states and crystallization processes take place mostly in modified stripes leaving the rest of the film in amorphous state. This leads to decrease of photoconductivity in nanocrystalline part of the film and its contribution to measured samples photoconductivity. Therefore measured photoconductivity and CPM spectra are determined mainly by weak modified amorphous part. This fact would explain both i) a-Si-like shape of spectral dependences of absorption coefficient of all treated films which were measured by CPM technique, based on photoconductivity measurements; and ii) overlap of “absorption shoulders” of films with different hydrogen content.

4. Conclusions

Structural, optical, electrical and photoelectric properties of a-Si:H films modified by ultrafast infrared laser radiation were investigated. By means of AFM measurements it was observed that femtosecond laser irradiation resulted in non-uniform a-Si:H structure modification. From Raman investigations the levels of crystalline volume fraction and relative hydrogen content in studied films were estimated. The dark conductivity of femtosecond laser treated a-Si:H films with crystalline volume fraction more than 13.4 % was found to increase by about 6 orders of magnitude compared to pristine a-Si:H, which was associated with appearance of nanocrystalline part contribution to charge carriers transport path through the film. Spectral dependences of absorption coefficient of laser treated a-Si:H films were explained in terms of hydrogen out-effusion and additional defect states formation in treated films during the laser processing. Hydrogen out-effusion minimization during the laser processing is suggested to be a potential remedy for improvements, which needs further investigation.

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Figure captions

Fig. 1. AFM images of pristine a-Si:H film (top left) and irradiated one with fluence of 60 mJ/cm² (top right) and its cross-sectional view (bottom).

Fig. 2. Raman spectra of a-Si:H films treated with different laser fluences. The inset shows the part of the Raman spectra corresponding to vibration mode of Si-H bonds.

Fig. 3. c-Si volume fraction (circles, dashed line) and relative H content change (squares, dotted line) in studied films against laser fluence. Lines are guides for eye.

Fig. 4. Dark conductivity (filled circles) and photoconductivity (open circles) of the samples as functions of laser fluence. Dashed lines are guides for eye.

Fig. 5. Spectral dependences of absorption coefficient of the samples, measured by constant photocurrent method, normalized to the value of absorption coefficient at $h\nu = 1.8$ eV.

Figure 1

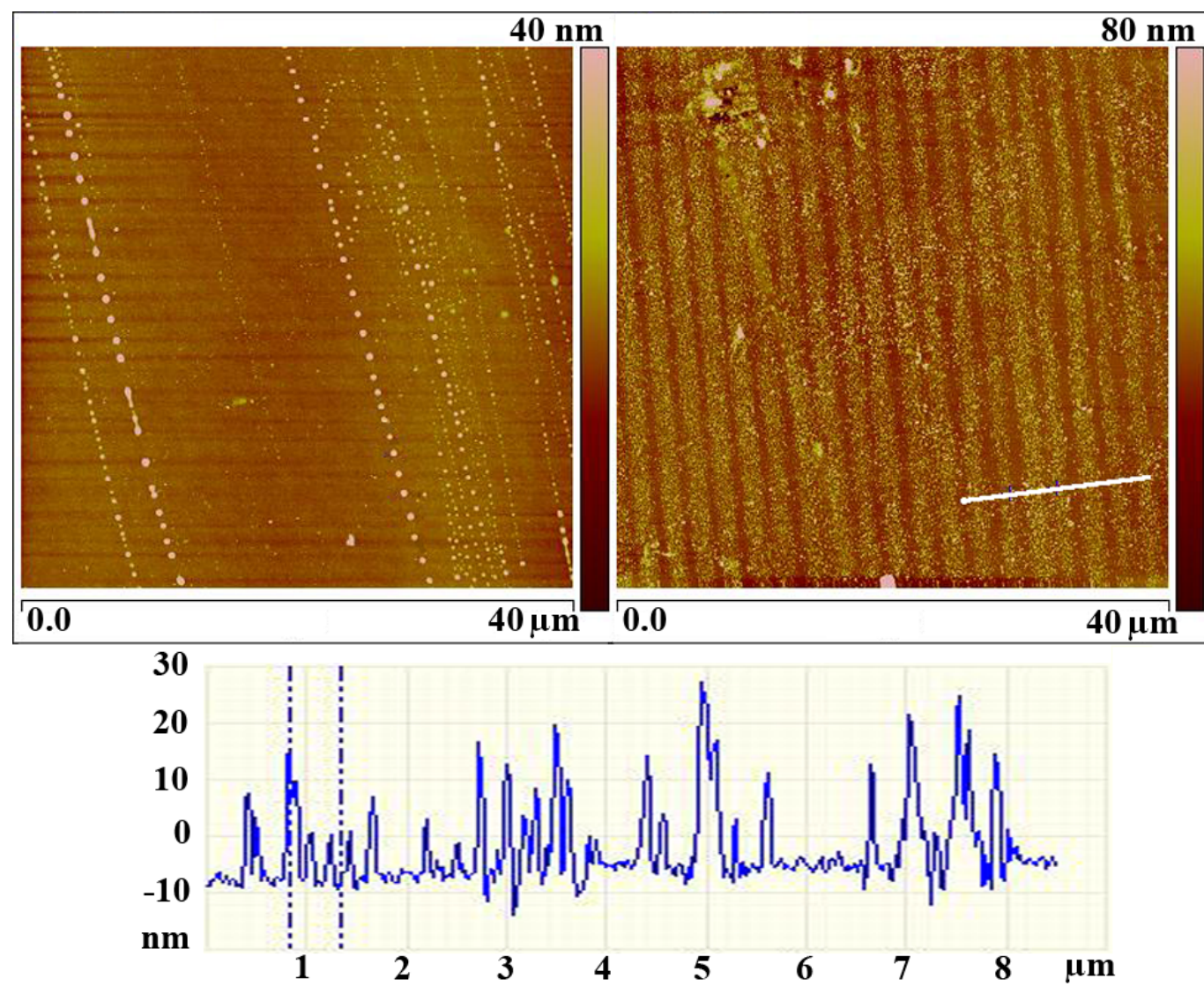


Figure 2

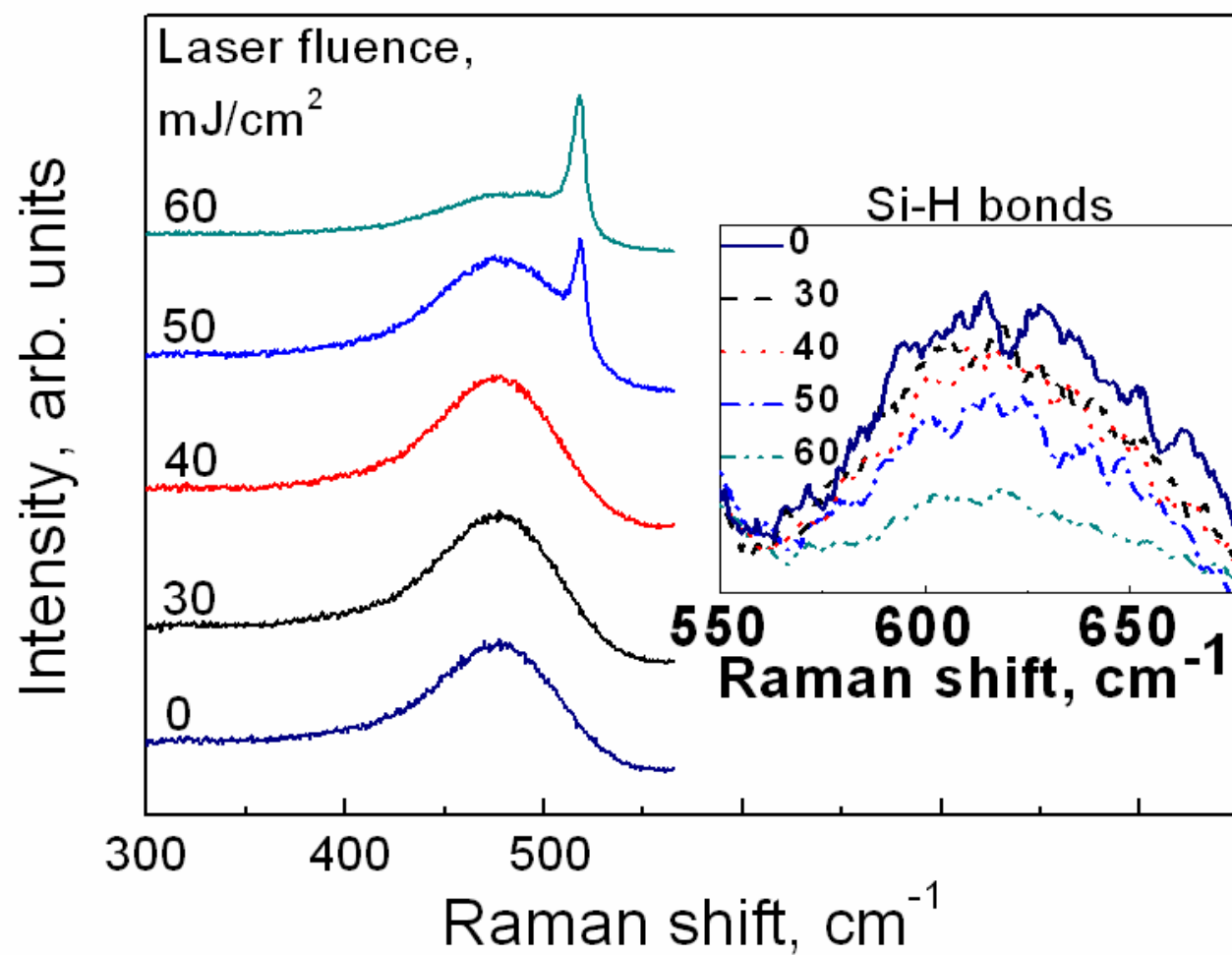


Figure 3

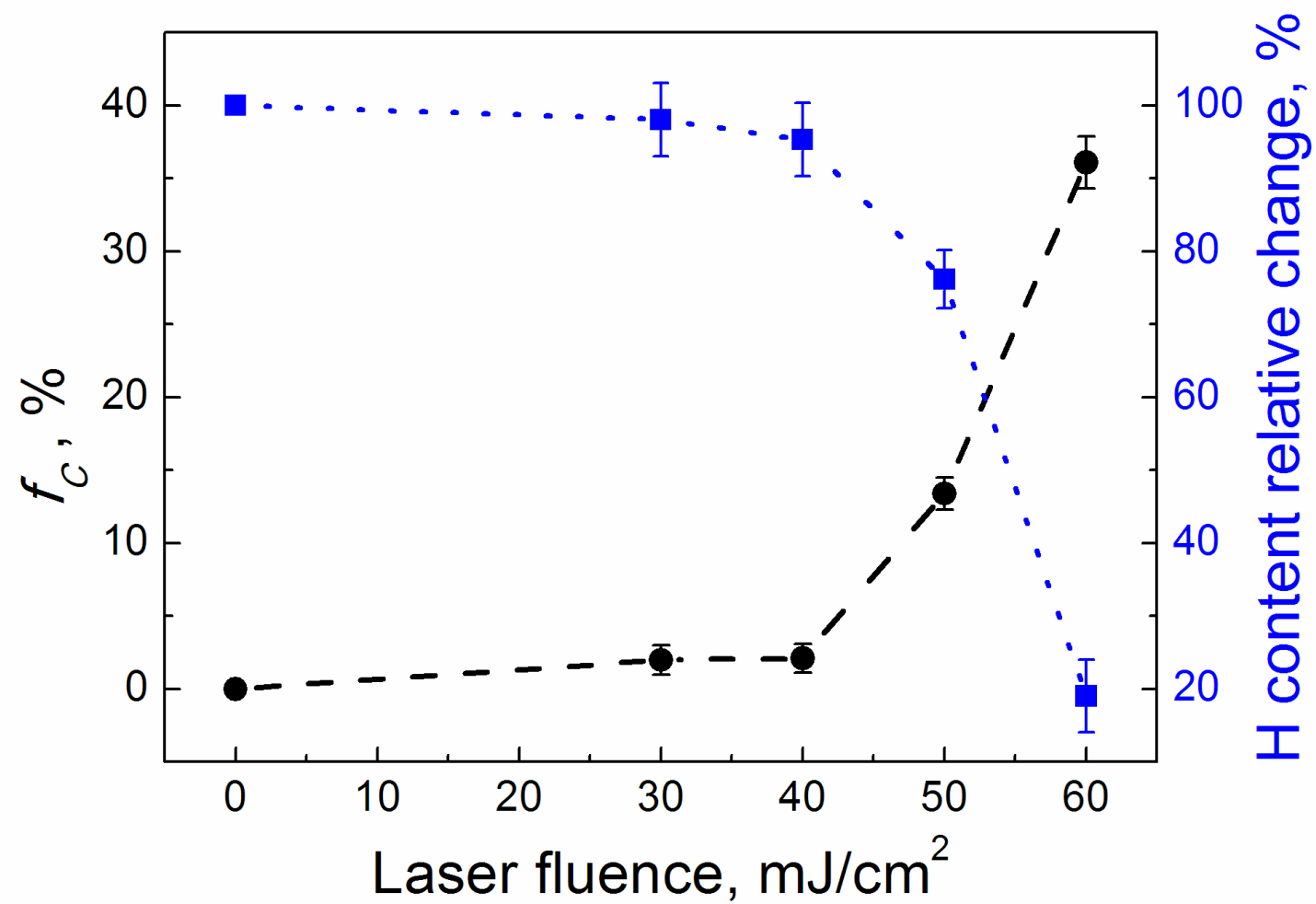


Figure 4

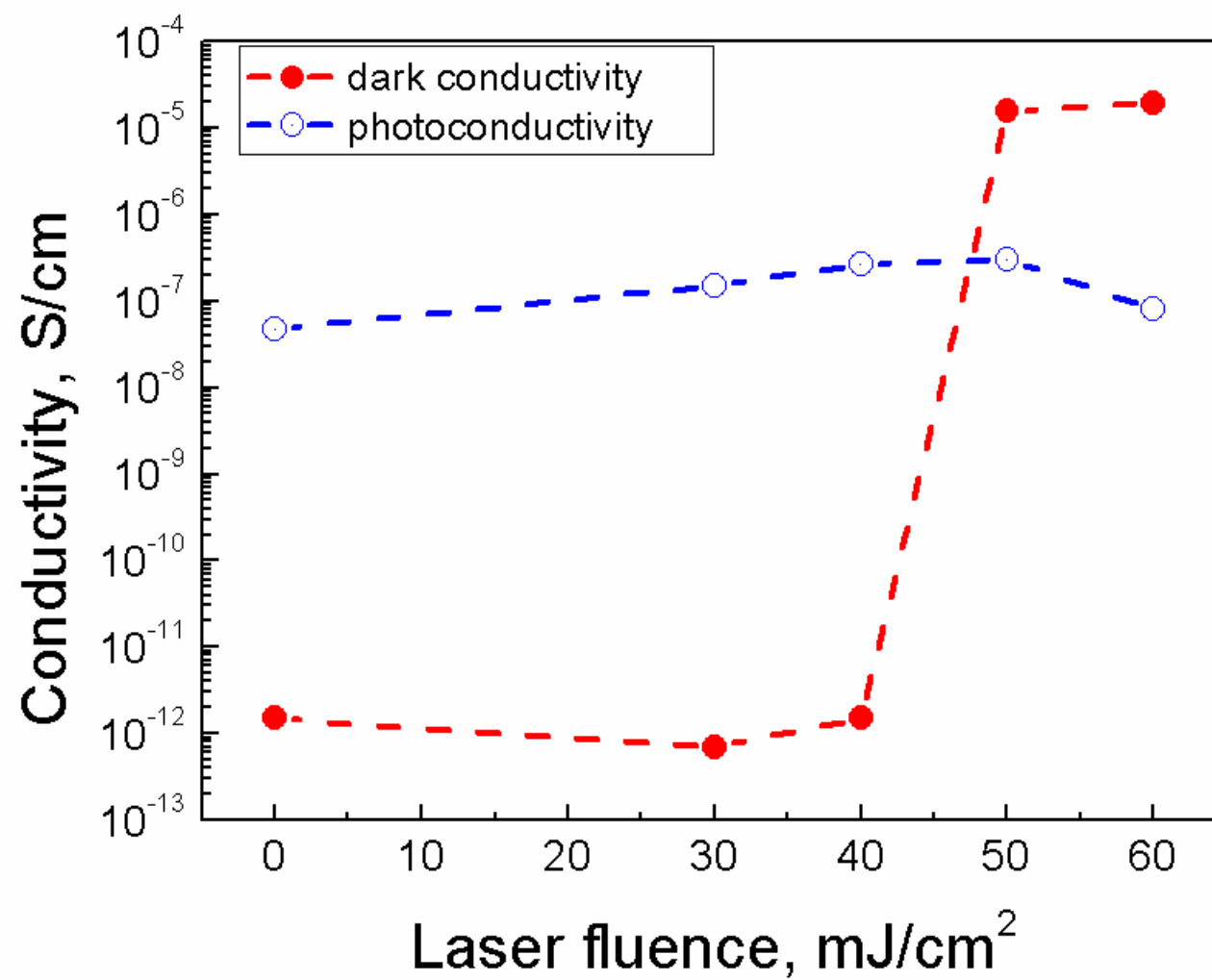
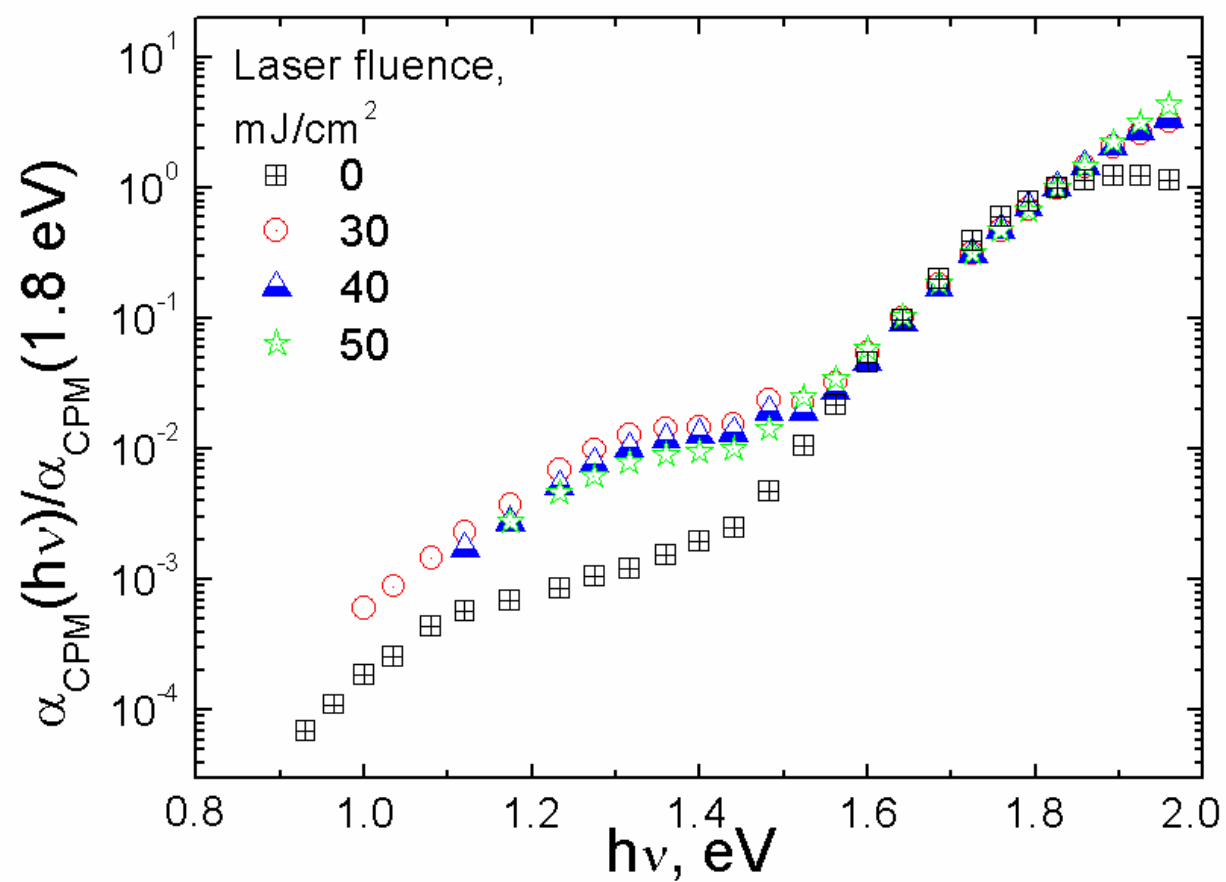


Figure 5



Highlights

- Structural, optical and electrical properties of laser modified a-Si:H were studied
- Volume fraction of Si nanocrystals in a-Si:H increased with applied laser fluence
- Laser modification is accompanied by hydrogen effusion from a-Si:H film
- Laser modification of a-Si:H leads to increase of dangling bonds concentration
- Conductivity of laser modified a-Si:H increases by about 6 orders of magnitude